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PROCESS FOR THE PRODUCTION OF ETHER ISOCYANATES

BACKGROUND OF THE INVENTION

5 The present invention relates to a process for the production of ether (poly)isocyanates by phosgenation of ether amines in the vapor phase.

Isocyanates containing ether groups or ether isocyanates are well known. (See, for example, Annalen der Chemie, 562 (1949), 83 ff).

10 However, these known ether-containing isocyanates are generally obtainable only in poor yield and low purity.

In the reactions of ether amines, chlorinated products are frequently obtained by splitting the ether (U.S. Patent 3,267,122). Thus, for example,  $\text{H}_2\text{N}(\text{CH}_2)_3\text{-O-(CH}_2)_4\text{-O-(CH}_2)_3\text{NH}_2$  is split into  $\text{OCN}(\text{CH}_2)_3\text{Cl}$  during the reaction with  $\text{COCl}_2$  (reference: Angew. Chem., A 59 (1949), 271).

Only aliphatic ether amines having HCl salts which are soluble in chlorinated hydrocarbons, for example,  $\text{C}_4\text{H}_9\text{-O-(CH}_2)_3\text{NH}_2$ , can be converted to ether isocyanates at temperatures below  $80^\circ\text{C}$  (Annalen der Chemie, 562 (1949), 105). The yield of this isocyanate is, however, only 86% of the theoretical yield. In such a process, it is necessary to convert the amine into the amine hydrochloride prior to the phosgenation. About 80% methoxypropylamine hydrochloride splits at  $140$  to  $150^\circ\text{C}$  in 1-chloronaphthalene with phosgene to form 3-chloropropyl isocyanate 25 (Annalen der Chemie, 562 (1949), 104).

Certain ether isocyanates can be obtained in yields of up to about 80% by simple base phosgenation. (See, for example, DE-A 1,154,092.) However, the products of such processes have very high residual chlorine contents (0.1%). Such a high chlorine content in the diisocyanate 30 frequently makes it difficult to use those products. For example, such chlorine-containing diisocyanates are not useful for the preparation of

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non-discoloring raw materials for coatings. The corresponding hydrochlorides of the amines or carbamates must be used in such processes. The handling of heterogeneous reaction mixtures of this type is, however, very difficult and is an obstacle to the smooth, economical  
5 production of the isocyanates.

(Poly)isocyanates containing ether groups are also obtainable by nucleophilic substitution of organic halides by metal cyanates. (See, for example, JP 50 036 424; Arch. d. Pharm., 302 (1969), 617; and DE-A 2,031,291) The accumulation of salts, the generally low conversion rates  
10 and the environmental problems encountered in these processes are obstacles to the industrial exploitation of this approach.

The reaction of ether (poly)amines with low-molecular weight alkyl isocyanates, subsequent thermal decomposition of the ureas formed and separation of alkylamine has also been proposed as a method for the  
15 preparation of ether (poly)isocyanates ("isocyanate interchange"; see, for example, DE-A 3,232,917). However, this method has several disadvantages. First, a by-product which must be disposed of is obtained. Second, considerable quantities of urea remain in the product, particularly when the ether (poly)isocyanates cannot be worked up by  
20 subsequent purification processes. Another disadvantage of this process is that the "isocyanate interchange" is a typical equilibrium reaction and is therefore difficult to carry out quantitatively.

Isocyanates containing ether groups can also be prepared by Curtius rearrangement of the corresponding carboxylic acid azides  
25 (J. Prakt. Chem., 335 (1993), 294 and the references cited therein), but only on a laboratory scale.

As is explained in DE-A 1,165,580, e.g., polyisocyanates containing ether groups are of great interest for use in paints and coatings.

Splitting the ether group in ether amines occurs more readily and  
30 completely at elevated temperatures. For example, phosgenation of 3-

methoxypropylamine in toluene below 110°C produces a mixture of 3-methoxypropyl isocyanate and 3-chloropropyl isocyanate. At elevated temperature (e.g., 140 to 150°C) in chloronaphthalene as solvent, however, substantially only 3-chloropropyl isocyanate is formed (Annalen  
5 der Chemie, 562 (1949), 83).

DE-A 1,793,329 discloses a cold phase-hot phase phosgenation in solution for the preparation of ether(poly)isocyanates. It is alleged that very little, if any, splitting of the ether occurs. However, the yields of isocyanate are only 60 to 75% of the theoretical yield. The chlorine  
10 content of the products, at 400 to 2000 ppm, is far too high for many applications, particularly for paint and coatings applications.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for the production of ether (poly)isocyanates.

15 It is also an object of the present invention to provide a simple process for the production of isocyanates containing ether groups.

It is another object of the present invention to provide a process for the production of high quality isocyanates containing ether groups.

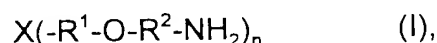
It is a further object of the present invention to provide a process  
20 for the production of high quality ether isocyanates in high yields without significant product loss through, for example, splitting of the ether groups.

These and other objects which will be apparent to those skilled in the art are accomplished by converting mono- and polyamines containing ether groups to the corresponding isocyanates in very good yields and in  
25 high purity, without splitting the ether group. This conversion is achieved by reacting an ether-containing amine in the vapor phase with phosgene in the vapor phase under applied pressure at a temperature in the range from 50 to 800°C, preferably from 100 to 550°C (depending on the boiling point of the amine), optionally in the presence of an inert carrier  
30 gas.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for preparing ether (poly)isocyanates from ether (poly)amines in which ether (poly)amines are reacted with at least the stoichiometric quantity, based on the NH<sub>2</sub> group(s), of phosgene or corresponding quantities of a material which generates phosgene, in the vapor phase close to or above the boiling point of the starting (poly)amine which boiling point is in the temperature range of from 50 to 800°C, preferably from 100 to 550°C, under applied pressure.

In the present invention, the ether amines which may be used include compounds represented by Formula (I)



in which

<p>X</p> <p>15    R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup></p> <p>20</p> <p>and</p> <p>n</p>	<p>represents H, NH<sub>2</sub> or C(R<sup>3</sup>)<sub>4-n</sub>,</p> <p>each represent the same or a different, optionally branched, optionally substituted (e.g., with Cl, Br), optionally heteroatom-containing (e.g., N, O, S) C<sub>1</sub>-C<sub>10</sub>alkyl, C<sub>3</sub>-C<sub>24</sub> cycloalkyl, C<sub>7</sub>-C<sub>24</sub> aralkyl, or C<sub>6</sub>-C<sub>24</sub> aryl radical, and R<sup>1</sup> may also represent a direct bond between X and the ether oxygen atom bonded to R<sup>2</sup>,</p> <p>represents 1, 2 or 3.</p>
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The process of the present invention may be carried out using known techniques. Suitable techniques are disclosed in EP-A 0,570,799 and DE-A 4,412,327. In these disclosed processes, the co-reactants are introduced into suitable reactors maintained at a temperature close to or above the boiling point of the starting amine or mixture of amines. The co-reactants are then mixed and reacted with one another. The temperature, depending upon the pressure, is generally between 50 and

800°C, preferably between 100 and 550°C. The process is generally carried out within a pressure range of from 10 mbar to 5 bar, preferably from 200 mbar to 3 bar.

Introduction of the reaction components during the vapor phase  
5 phosgenation may optionally take place in the presence of inert additives such as carrier gases. The carrier gases used may be nitrogen, argon or other inert gases and vapors of commercially available solvents such as chlorobenzene, dichlorobenzenes, xylenes, chloronaphthalenes and decahydronaphthalene.

10 The phosgene used in the phosgenation reaction is used in a stoichiometric amount or in stoichiometric excess, determined on the basis of the number of primary amino groups in the amine starting material. A quantity of phosgene amounting to from 100 to 300% of the theoretical quantity, preferably from 100 to 200% of the theoretical  
15 quantity, is generally sufficient.

After the reaction with phosgene, the ether isocyanates are recovered by cooling the gas stream to a temperature above the decomposition temperature of the corresponding intermediate carbamic acid chlorides. The ether isocyanate may then be isolated in pure form  
20 by known processes such as distillation, crystallization, extraction or film distillation, or recovered as raw product (solution).

The amine starting materials which are converted into the corresponding isocyanates by the process of the present invention may be obtained by a number of known processes. One suitable known  
25 process is alkoxylation of water or of other, optionally polyfunctional, OH-functional compounds such as alcohols, phenols and/or carboxylic acids and subsequent amination (for example, FR-A 1 361 810). Another suitable process for producing the amine starting material is polymerization of tetrahydrofuran and, optionally after further reaction  
30 with alkylene oxide, subsequent treatment as described in FR-A-1 361

810. Suitable amine starting materials may also be produced by cyanoethylation of water and subsequent hydrogenation to form bis(3-aminopropyl)ether (DRP 731 708) or by cyanoethylation of other, optionally polyfunctional, OH-functional compounds (particularly diols and triols) and subsequent hydrogenation.

The usefulness of mono- and polyamines containing ether groups in the phosgenation of the present invention is determined essentially by the vapor pressure of the amine at the applied pressure. In the case of particularly high-boiling compounds, it may be advantageous to introduce the amine into the phosgenation reaction as an azeotrope with other substances, or to use a carrier gas for the introduction of the amine component into the reaction chamber.

Typical examples of suitable (poly)amines of Formula (I) which may be used alone or as mixtures include: alkyl aminoalkyl ethers such as aminomethyl methyl ether, aminomethyl ethyl ether, aminomethyl propyl ether (as well as isomers), 1-aminoethyl methyl ether, 2-aminoethyl methyl ether, and aminopropyl methyl ether (as well as isomers); diamino-oxoalkanes such as 1,1'-bis(aminomethyl) ether, 1,1'-bis(aminoethyl) ether, 1,2'-bis(aminoethyl) ether, 2,2'-bis(aminoethyl) ether and technical mixtures of the three latter diamines, bis(aminopropyl) ether (all isomers, optionally as a mixture), diamino(poly)oxoalkanes such as 1,8-diamino-1,5,8-trimethyl-3,6-dioxaoctane, 1,11-diamino-1,5,8,11-tetramethylundecane and all isomers of the two latter compounds having vicinal O-N bonding in pure form or as a mixture (for example, as commercial Jeffamine D 230), 1,8-diamino-3,6-dioxaoctane (for example, as commercial Jeffamine EDR 148), 1,10-diamino-4,7-dioxadecane, 1,12-diamino-4,9-dioxadodecane, 1,14-diamino-3,10-dioxatetradecane, and 1,13-diamino-4,7,10-trioxatridecane; triamino(poly)oxoalkanes such

as 1,7-diamino-2,6-dioxo-4-aminomethoxyheptane, 1-amino-2-oxa-3,3-bis(aminomethoxy)hexane, 1,9-diamino-3,7-dioxo-5-(1-amino-2-ethoxy)-nonane, 1-amino-3-oxa-4,4'-bis(1-amino-2-ethoxy)heptane, 1,11-diamino-4,8-dioxo-6-(1-amino-5-oxobutyl)undecane, 1-amino-4-oxa-5,5-bis(1-amino-5-oxobutyl)octane and mixtures of the above-mentioned monoamines, diamines and triamines.

The mixture of isomers composed of 2-(2-isocyanatopropoxy)-1-propyl isocyanate, 1,1'-oxydi-2-propyl isocyanate and 2,2'-oxydi-1-propyl isocyanate ("dipropylene glycol diisocyanate", mixture of isomers) prepared by the process of the present invention is new.

The ether isocyanates prepared by the process of the present invention are valuable raw materials for the production of polyurethanes (optionally foamed), adhesives, coating materials, emulsifiers, thickeners, oligomeric isocyanate modification products (e.g., polyisocyanates containing uretdione, isocyanurate, carbodiimide, biuret, urethane and allophanate groups), and auxiliary substances which are used, for example, for imparting wet strength to paper and other cellulose products. These ether isocyanates are useful as raw materials for the production and/or formulation of active substances and pharmaceuticals (DE-A 3,232,917).

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight, unless otherwise specified.

#### EXAMPLES

##### 25 Example 1

2-(2-isocyanatopropoxy)-1-propyl isocyanate, 1,1'-oxydi-2-propyl isocyanate and 2,2'-oxydi-1-propyl isocyanate ("dipropylene glycol diisocyanate", mixture of isomers) were prepared by the procedure described below.

The apparatus in which the reaction was conducted included a mixer tube heated to 400°C which was 2.5 mm in diameter and 17.5 mm in length having a condensation stage arranged in tandem and a connected  $\text{COCl}_2$  adsorption tower filled with activated carbon.  $\text{COCl}_2$ , which had been heated to 420°C at 950 mbar in a heat exchanger connected in front, flowed continuously at a rate of 2.5 mol/h through a nozzle projecting into the mixer tube. Simultaneously, a mixture of amines heated to 320°C, obtained by catalytic amination under pressure of technical dipropylene glycol (approx. 50% 2-(2-hydroxypropoxy)-1-propanol, approx. 40% 1,1'-oxydi-2-propanol and approx. 10% 2,2'-oxydi-1-propanol) having a boiling range of 72 to 78°C at a pressure of 7.5 mbar, was introduced at a feed rate of 1 mol/h, together with dry nitrogen at a rate of 0.1 mol/h as diluent, into the reaction chamber via the annular passage between the nozzle and the mixer tube. A pressure of approx. 350 mbar was maintained in the mixer tube by applying a reduced pressure at the end of the condensation stage. That is, the reaction mixture leaving the reaction chamber was passed in a condensation stage through 1,2-dichlorobenzene, which was maintained at 150 to 160°C. Here the selective condensation of the diisocyanates formed took place. In the adsorption tower,  $\text{COCl}_2$  was separated from the gas mixture passing through the scrubbing stage and containing nitrogen, HCl and excess  $\text{COCl}_2$ . The mixture of diisocyanates was recovered in a pure state by distillation ( $K_p = 95^\circ\text{C}/0.05 \text{ mbar}$ ,  $n_D = 1.4393/20^\circ\text{C}$ ) and descended as a colorless liquid having an NCO content, titrated in accordance with DIN 53 185, of 45.4% (theoretical: 45.6%). The yield of the pure, distilled mixture of diisocyanates was 98.2% of the theoretical yield, based on the mixture of diamines used, with a purity of 99.7% as determined by gas chromatography and a content of hydrolyzable chlorine of 43 ppm.

30 Example 2



1,8-diisocyanato-3,6-dioxaoctane was prepared in accordance with the procedure described below.

2.5 kg (16.87 mol) of 1,8-diamino-3,6-dioxaoctane which is commercially available from Aldrich (also known as Jeffamine EDR 48) was converted into 1,8-diisocyanato-3,6-dioxaoctane and isolated in the manner specified in Example 1.

Yield: 3360 g = 99.5% of the theoretical yield, purity (GC): 99.8%, NCO content in accordance with DIN 53 185: 42.0% (theoretical: 42.0%), Hydrolyzable chlorine content: 48 ppm. Kp: 95°C/0.5 mbar.

10 Example 3

1,12-diisocyanato-4,9-dioxadodecane was prepared from 2.5 kg (12.24 mol) of 1,12-diamino-4,9-dioxadodecane (commercially available from Aldrich) and isolated in the manner specified in Example 1.

Yield: 3056 g = 97.4% of the theoretical yield, purity (GC): 99.5%, NCO content in accordance with DIN 53 185: 32.9% (theoretical: 33.0%), Hydrolyzable chlorine content: 34 ppm. Kp: 83°C/0.2 mbar.

Example 4

1,3-bis(3-isocyanatopropoxy)-2,2-dimethyl propane was prepared from 2.5 kg (11.45 mol) of 1,3-bis(3-aminopropoxy)-2,2-dimethyl propane (commercially available from Aldrich) and isolated in the manner specified in Example 1.

Yield: 3067 g = 99.1% of the theoretical yield, purity (GC): 99.8%, NCO content in accordance with DIN 53 185: 31.0% (theoretical: 31.1%), Hydrolyzable chlorine content: 24 ppm. Kp: 108°C/0.1 mbar.

25 Example 5

3-methoxypropyl isocyanate was prepared from 1,000 g (11.2 mol) of 3-methoxypropylamine (commercially available from Aldrich) was converted into the isocyanate and isolated in the manner specified in Example 1.

Yield: 1250 g = 96.8% of the theoretical yield, purity (GC): 99.1%, NCO content in accordance with DIN 53 185: 36.5% (theoretical: 36.50%), Hydrolyzable chlorine content: 44 ppm. Kp: 55°C/20 mbar.

The identity of all the compounds produced in these Examples  
5 was deduced from IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and mass spectroscopic analyses and from the results of elemental analysis.

Comparative examples (liquid phosgenation)

440 g of monochlorobenzene were mixed at 5°C with 330 g of phosgene in a four-necked mixing flask equipped with reflux condenser,  
10 internal thermometer, dropping funnel and inlet tube. Then a solution of 71.5 g of the mixture of diamines specified in Example 1 in 900 g of monochlorobenzene was added dropwise over a period of 90 min.

The reaction mixture was then slowly heated, with stirring, to an internal temperature of 90°C with simultaneous introduction of phosgene  
15 (approx. 1 mol/h) and maintained at this temperature for several hours. It was not possible to achieve a complete elucidation of the reaction mixture. After blowing off of the excess phosgene with nitrogen, filtration and working up by distillation, 19.5 g (19.6% of the theoretical yield) of a slightly colored liquid was obtained, having a boiling range of 80 to  
20 85°C/0.07 mbar and an NCO content in accordance with DIN 53 185 of 45.2%.

Neither varying the solvent (1,2-dichlorobenzene (34% theoretical yield) and toluene (22.3% theoretical yield)) nor converting the mixture of  
25 diamines into the dihydrochloride and bis(carbamate) (15.3% and 27.6% yields, respectively) increased the yield of diisocyanate substantially. The residual chlorine content of the product was in no case below 0.1%.

Further examples of phosgenations of ether diamines in the liquid phase are described, for example, in Annalen der Chemie, 562 (1949), 6 ff; DE-A 1,154,092; JP 4,027,365; FR 1,578,622.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of

5 the invention except as it may be limited by the claims.